[CONTRIBUTION NO. 99 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Reactions of Free Radicals Formed from Thermal Decomposition of Acetyl Peroxide

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On the assumption[2] that the decomposition of acetyl peroxide gives rise to methyl radicals, the object of the present work was to compare the relative reactivities of several solvents with these radicals for comparison with corresponding reactivities toward the long-chain substituted benzyl and primary alkyl radicals which occur in polymerizing styrene[3] and ethylene.[4]

Previous work[5] has shown that the thermal decomposition of acetyl peroxide in the absence of a solvent yields chiefly methane, ethane, and carbon dioxide, but small amounts of oxygen (1%), carbon monoxide (1.5–3.0%), and ethylene (*ca.* 1%) were also obtained. In the present work only the major products were determined.

The general plan was to decompose acetyl peroxide thermally in a mixture of carbon tetrachloride with a solvent which did not contain chlorine. The carbon tetrachloride could furnish only a chlorine atom and the other solvent only a hydrogen atom for reaction with the radical. The methane–methyl chloride mixture obtained would measure the relative abilities of the two solvents to transfer an atom to the methyl radical. By comparing each solvent with carbon tetrachloride the relative reactivities of the chlorine-free solvents could be determined.

Experimental

Solvents were reagent grade commercial materials which were purified by fractional distillation.

Acetyl peroxide was prepared from acetic anhydride and sodium peroxide in carbon tetrachloride maintained at $<15°$ by the addition of crushed ice.[6] The organic layer was separated, washed with distilled water, and diluted with an equal volume of *n*-pentane. Chilling to $-78°$ produced white crystals, from which the liquors were removed with a sintered-glass filter stick. Two more recrystallizations from a carbon tetrachloride-*n*-pentane mixture were performed before the acetyl peroxide was dissolved in fresh carbon tetrachloride and dried over Drierite. Yields averaged 55–60% of theory.

For use, an aliquot of this stock solution was evaporated *in vacuo* at 0° to obtain the peroxide in a pure dry state.[7] The dry peroxide was sublimed *in vacuo* into a clean dry flask, weighed, and dissolved in a weighed amount of carbon tetrachloride. Aliquots of this solution were diluted with the requisite volumes of solvents.

Reaction mixtures were prepared in tubes fitted with a side arm ending in a 10/30 ₮ male joint and capillary. They were degassed three times at liquid nitrogen temperature at $< 10^{-3}$ mm. and sealed. Decomposition of the peroxide was carried to completion by heating for sixteen hours at 100° in tubes at least 80% filled with liquid.

Analysis of the gaseous products was carried out in the apparatus shown in Fig. 1. The reaction tube was attached to the system at T and the connection evacuated. With A closed, and B open, the capillary on the reaction tube was snapped by turning the stirrup S. With intermittent opening of B to allow gases to escape into the liquid nitrogen trap, N, the reaction solution was distilled into R and refluxed for a few minutes to insure complete removal of gas into N.

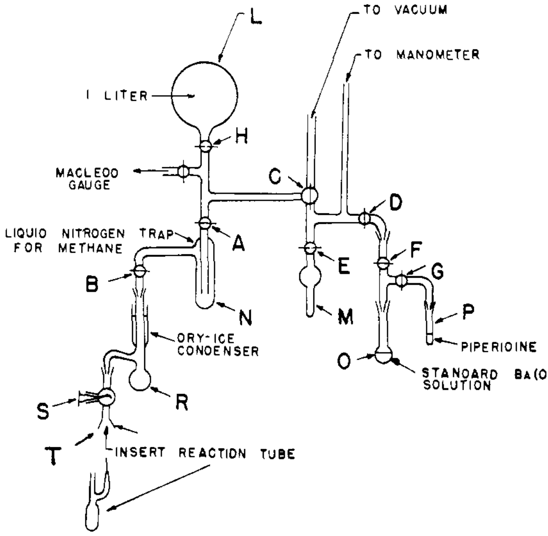

Fig. 1.—Gas analysis apparatus.

With B and C closed to isolate the left-hand part of the system, the methane was measured by allowing the gases and condensate at liquid nitrogen temperature to expand repeatedly into the bulb L and reading the pressure on a calibrated McLeod gage (Model J4140, Scientific Glass Apparatus Co.). Quantities as small as 0.001 millimole could be measured. After all of the methane was metered out, the remaining gases were separated from traces of solvent by means of several distillations from the trap N into the bulb M. The final distillation was carried out with the trap at $-78°$. With C and D closed the gases carbon dioxide, ethane, and methyl chloride were measured in a calibrated manometer before condensing on a standard solution of barium hydroxide (about 0.2 molar in both barium hydroxide and barium chloride) in bulb O. With F and G closed, this section of the apparatus was detached from the main part, and the barium hydroxide solution warmed to 30° and shaken vigorously. The operation of freezing, thawing, and shaking was carried out three times in all to ensure complete removal of carbon dioxide, which was determined by titrating excess barium hydroxide to a phenolphthalein end-point with 0.1 *N* hydrochloric acid.

The remaining gases, C_2H_6 and CH_3Cl, were distilled through G into tube P, containing 1 cc. piperidine which was sealed off and heated for 1 hr. at 100°. The methyl-

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(1) Present address, Dow Chemical Company, Midland, Michigan. This paper was presented before the Organic Division at the St. Louis Meeting of the American Chemical Society, September 8, 1948.

(2) Kharasch and Gladstone, THIS JOURNAL, **65**, 15 (1943); Kharasch, McBay and Urry, *ibid.*, **70**, 1269 (1948); and other papers.

(3) (a) Gregg and Mayo, *ibid.*, **70**, 2373 (1948); (b) Mayo, *ibid.*, 3689; (c) Gregg and Mayo, Discussions of the Faraday Soc., **2**, 328 (1947); (d) Gregg and Mayo, unpublished work.

(4) (a) Little, Hartzel, Guenther and Mayo; (b) Little, Stiteler, Guenther, and Mayo, papers to be submitted to THIS JOURNAL from this Laboratory.

(5) Walker and Wild, *J. Chem. Soc.*, 1132 (1937).

(6) Gambarjan, *Ber.*, **42**, 4010 (1909).

(7) Acetyl peroxide was isolated in not more than 1–2 g. quantities behind a safety shield. No difficulty was encountered with this procedure. However, attention is called to a warning published by L. P. Kuhn, *Chem. Eng. News*, **26**, 3197 (1948).

TABLE I

DECOMPOSITION PRODUCTS FROM 2 MILLIMOLES OF ACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 100°
(ALL QUANTITIES ARE IN MILLIMOLES)

Run	Ac_2O	CCl_4	Total gas	CH_4	CO_2	C_2H_6	CH_3Cl	$CH_4 + CH_3Cl + 2\ C_2H_6$	CH_4/CH_3Cl
198	...	200	4.877	0.202	2.939	0.166	1.570	2.104	0.129
199	...	200	4.175	.520	2.694	.087	0.874	1.568	.595
189	0.4	20	4.936	.274	3.057	.325	1.280	2.204	.214
217	.4	60	4.901	.131	3.004	.451	1.315	2.348	.0996
218	.4	60	4.673	.123	2.914	.376	1.260	2.135	.0976
219	.4	200	4.9092	.0742	3.084	.121	1.630	1.9462	.0455
197	.4	200	5.087	.0722	2.904	.316	1.795	2.4992	.0403
221	.4	600	4.6768	.0628	2.879	.215	1.520	2.0128	.0418
222	.4	600	4.9518	.0628	2.844	.389	1.656	2.4968	.0379

piperidinium chloride was destroyed by evaporating to dryness in a caustic solution and the original methyl chloride determined by a Volhard titration of chloride ion. Ethane was determined by difference, and its determination is therefore most subject to error, particularly from incomplete removal of low-boiling solvents.

This method determines traces of oxygen and carbon monoxide as methane and ethylene as ethane. However, the proportions of these gases are apparently insignificant.

The Effect of Acetic Anhydride on the Decomposition of Acetyl Peroxide in Carbon Tetrachloride.—Rate studies on the decomposition of acetyl peroxide in mixtures of carbon tetrachloride and acetic anhydride were carried out in an unsuccessful effort to understand the effect of the anhydride. The decomposition was followed by reaction of the remaining peroxide with potassium iodide in glacial acetic acid and titration of the liberated iodine with 0.05 *N* thiosulfate.[8] With 0.5 *M* peroxide in 100% carbon tetrachloride, the decomposition follows a first order law closely through 90% reaction and has a first order rate constant of 0.0002 min.$^{-1}$ at 60° and 0.044 min.$^{-1}$ at 100°, corresponding to an activation energy of 33.4 kcal./mole. In mixtures of acetic anhydride and carbon tetrachloride, the rate of decomposition is faster. As acetic anhydride is added to the reaction mixture, the initial rate of decomposition increases, at first without a detectable change in order, later with a change of which the interpretation is uncertain, and finally with a change corresponding to a second order reaction. Thus, with 5 mole % acetic anhydride (considerably more than was used in experiments run for reaction products) the first order rate constant at 100° is 0.051 min.$^{-1}$, a 15% increase. Deviations from a first order reaction with 20 mole % acetic anhydride seem due to an increase in the initial rate and then a retardation near the end by the decomposition products, but these conclusions have not been tested. The data for 50 mole % acetic anhydride do not fit a first order reaction but apply more nearly to a second order curve, the second order rate constant being about 1.68 l./mole/min. The data reveal no obvious interpretation for the effect of the anhydride.

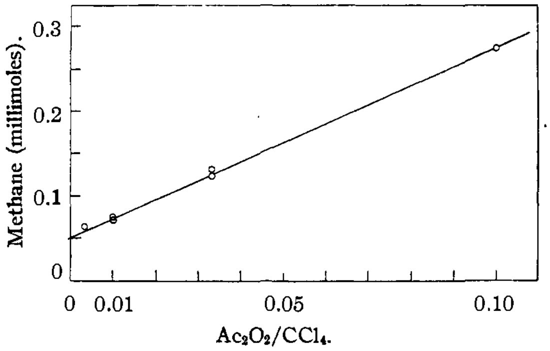

Fig. 2.—Effect of dilution on yield of methane from 2 millimoles of acetyl peroxide at 100°.

Results and Discussion

The Decomposition of Acetyl Peroxide in Carbon Tetrachloride.—The decomposition of acetyl peroxide in carbon tetrachloride alone gave some methane along with carbon dioxide, methyl chloride, and ethane. The first two experiments in Table I illustrate results obtained under such conditions: results were not at all reproducible, and the ratio of methane to methyl chloride obtained varied widely and unpredictably. Tests of the effect of several other compounds on the decomposition showed that the addition of a small proportion of acetic anhydride *reduced* and made reproducible the proportion of methane formed. Although no explanation for this effect of acetic anhydride was found, the desired reproducibility appears with only a very small proportion of the anhydride, and the remaining experiments in Table I were carried out with 20 mole % of acetic anhydride on the acetyl peroxide, 0.07 to 2 mole % on the carbon tetrachloride.

Data on acetyl peroxide decomposition in chloroform, cyclohexane, and toluene show that acetic anhydride has no effect on the gases obtained, the results being reproducible in the absence of anhydride in these hydrogen-containing solvents.

Table I and Fig. 2 show that the amount of methane produced increases directly with the acetyl peroxide:carbon tetrachloride ratio in the feed and that at infinite dilution about 0.025 mole of methane should be produced per mole of peroxide. This minimum of methane presumably comes from interaction of pairs of radicals from the decomposition before they can escape into the solvent, while additional methane formed in more concentrated solutions of peroxide must come from the reaction of free radicals with acetyl peroxide molecules.

In order to determine non-gaseous products, 0.2 mole of acetyl peroxide was decomposed in 2 liters (20.7 moles) of carbon tetrachloride at reflux without added acetic anhydride. Gases were measured as described above and other products were identified after fractional distillation of the residue. The essential data are summarized in Table II.

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[8] Liebhafsky and Sharkey, THIS JOURNAL, 62, 190 (1940).

TABLE II

DECOMPOSITION PRODUCTS FROM 0.2 MOLE OF ACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 76°

Product	Found millimoles	Millimoles of fragments accounted for ·CH_3	CO_2
Methane	10–16	20–32	...
Ethane	34	68	...
Methyl chloride	229	229	...
Carbon dioxide	317	.....	317
Methyl acetate	32	64	32
Hexachloroethane	105	.....	...
		381–393	349

They show that 95–98% of the methyl residues and 87% of the theoretical carbon dioxide are accounted for. The remainder of the products, not readily identified by the present method, must arise from various side reactions; *e. g.*, phosgene was detected but not measured quantitatively, and the formation of a methane molecule may eliminate another potential methyl radical and perhaps a carbon dioxide molecule as well. Test for unsaturation was negative.

The Decomposition of Acetyl Peroxide in Carbon Tetrachloride–Solvent Mixtures.—The experiments in Table III were carried out for sixteen hours at 100° with a total solvent–acetyl peroxide–acetic anhydride ratio of 100:1:0.2, and usually with two different proportions of carbon tetrachloride. From Fig. 2 it is seen that in carbon tetrachloride alone, at the concentration of peroxide used in these experiments, 0.035 mole of methane per mole of peroxide is formed from reactions of radicals with peroxide molecules or fragments. Hence, in measuring the relative reactivity of mixed solvents, this quantity is subtracted from the measured quantity of methane. Since the solutions are very dilute, the constant correction cannot be seriously in error. The corrected quantity of methane is then ascribed to the reaction of radicals with the chlorine-free solvent and the methyl chloride is ascribed to reaction with carbon tetrachloride. The relative reactivity value is obtained by dividing the corrected methane:methyl chloride ratio by the ratio of chlorine-free solvent to carbon tetrachloride in the feed. For chloroform a slight correction is necessary for the amount of methyl chloride contributed by reaction of the chlorine atoms of the chloroform with the free radicals. Experiments 210, 215 and 216 (Table III)

TABLE III

DECOMPOSITION PRODUCTS OF 2 MILLIMOLES OF ACETYL PEROXIDE IN SOLVENT MIXTURES AT 100°
(ALL QUANTITIES ARE IN MILLIMOLES)

Run	CCl_4	Co-solvent Name	Co-solvent Amt.	Total gas	CH_4	CO_2	C_2H_6	CH_3Cl	$CH_4CH_3Cl + 2\ C_2H_6$	CH_4/CH_3Cl[a]	Reactivity
227	50	Benzene	150	5.157	0.230	3.099	0.455	1.373	2.513	0.1166	0.0389
228	50	Benzene	150	5.157	.232	3.069	.466	1.390	2.554	.1166	.0389
236	20	Benzene	180	5.147	.437	3.094	.450	1.066	2.403	.344	.0382
253	50	Methyl benzoate	150	4.548	.213	2.894	.589	0.852	2.243	.1915	.0638
254	100	Methyl benzoate	100	4.7985	.1375	3.039	.522	1.100	2.2815	.0614	.0614
238	150	Acetone	50	4.775	.247	2.944	.277	1.307	2.108	.1354	.406
239	100	Acetone	100	5.263	.582	3.039	.403	1.238	2.626	.414	.414
240	100	Acetone	100	5.245	.524	3.007	.512	1.205	2.753	.377	.377
211	100	Toluene[b]	100	4.951	.668	2.744	.704	0.835	2.911	.716	.716
212	100	Toluene	100	4.897	.674	2.846	.577	0.800	2.628	.755	.755
214	160	Toluene	40	4.962	.316	2.880	.495	1.271	2.577	.193	.768
244	150	Octene-1	50	4.532	.640[c]	3.039	.318	0.535	1.811	1.065	3.19
245	100	Octene-1	100	4.382	.852[c]	2.974	.326	.230	1.734	3.35	3.35
246	100	Octene-1	100	4.353	.842[c]	2.964	.307	.240	1.696	3.22	3.22
233	50	Cyclohexane	150	5.818	2.288	3.029	.351	.150	3.140	14.78	4.93
234	50	Cyclohexane	150	5.876	2.356	3.004	.356	.160	3.228	14.28	4.76
223	100	Chloroform	100	5.630	2.130	2.979	.314	.207	2.965	12.3	12.3
224	100	Chloroform	100	6.662	2.530	3.179	.683	.270	4.166	11.1[d]	11.1
225	160	Chloroform	40	5.394	1.554	2.974	.243	.623	2.663	2.50[d]	10.0
226	160	Chloroform	40	5.250	1.590	2.844	.236	.580	2.642	2.76[d]	11.0
210	...	Chloroform	200	6.355	2.845	2.899	.543	.068	3.999	.....	.....
215	...	Chloroform	200	5.692	2.440	2.759	.463	.030	3.396	.....	.....
216	...	Chloroform	200	6.395	2.850	2.825	.673	.047	4.243	.....	.....
247	100	Methyl acetate	100	6.773	2.931	2.979	.731	.132	4.525	21.7	21.7
248	100	Methyl acetate	100	6.784	2.941	3.109	.596	.138	4.271	20.8	20.8
252	160	Methyl acetate	40	6.035	2.362	3.124	.139	.410	3.050	5.59	22.4
251	160	*n*-Butyraldehyde	40	9.370	2.769	3.43	2.78	.39	....	......	....[e]

[a] After subtracting 0.07 millimole of methane from quantity found, for interaction of peroxide fragments with each other or other peroxide molecules.

[b] No acetic anhydride present; 0.4 millimole present in all other experiments.

[c] Gas other than methane present.

[d] After subtracting 0.019 millimole of methyl chloride formed per millimole (corrected) of methane found.

[e] In the butyraldehyde experiment, large quantities of gases considered to be carbon monoxide and propane from the characteristic chain decomposition of *n*-butyraldehyde were produced; *cf.* Leighton, *et al.*, THIS JOURNAL, **59**, 1843 (1937).

show that in chloroform the decomposition of acetyl peroxide yields an average of 0.019 mole of methyl chloride per mole of methane (corrected) and this correction for methyl chloride was made before calculation of the relative reactivity of chloroform.

The yields of gaseous products will now be considered. Acetyl peroxide decomposes into two acetate radicals or their equivalent in methyl radicals and carbon dioxide. The following reactions may then occur, peroxide decomposition induced by free radicals being neglected (Table I and Fig. 2)

$$\begin{array}{c} \mathrm{AcO}\cdot \\ \text{or} \\ \mathrm{Me}\cdot \\ + \\ \mathrm{CO_2} \end{array} \left\{ \begin{array}{llll} + \text{ solvent} & \longrightarrow & \mathrm{MeH}\ (\text{or MeCl}) & \\ & & \quad + \mathrm{CO_2} + \mathrm{R}\cdot & (1) \\ & \longrightarrow & \mathrm{AcOH} + \mathrm{R}\cdot & (1a) \\ + \mathrm{AcO}\cdot & \longrightarrow & \mathrm{AcOMe} + \mathrm{CO_2} & (2) \\ \quad (\text{or } \mathrm{Me}\cdot + \mathrm{CO_2}) & \longrightarrow & \mathrm{EtH} + 2\mathrm{CO_2} & (2a) \\ + \mathrm{R}\cdot & \longrightarrow & \mathrm{MeR} + \mathrm{CO_2} & (3) \\ & \longrightarrow & \mathrm{AcOR} & (3a) \\ + \text{ unsaturated} & \longrightarrow & \mathrm{R}\cdot + \mathrm{CO_2} & (4) \\ \quad \text{solvent} & \longrightarrow & \mathrm{R'}\cdot & (4a) \end{array} \right.$$

Table III shows a surprisingly uniform release of about 75% of the theoretically possible carbon dioxide, indicating the adequacy of the analytical method. This value also proves that if peroxide yields equal quantities of methyl and acetate radicals,[2] then a substantial portion of the latter subsequently lose carbon dioxide.

Reaction (1) is the only one above yielding methane or methyl chloride and it yields an equivalent quantity of carbon dioxide. Methyl acetate, shown in the next section to be the most reactive solvent, reacts according to (1) to the extent of 75%, the other 25% reacting by all other courses together, mostly those (1a, 3a) not liberating carbon dioxide. In carbon tetrachloride alone, and in its mixtures with most of the less reactive solvents (top of Table III), only 35–40% of the radical pairs react by (1), so that more must necessarily react by the other courses: about 10% by (2a), 25–30% by (2 + 3) and 25% by (1a + 3a). Chloroform and cyclohexane are intermediate in behavior. This correlation between reactivity and Reaction (1) also appears with changing feed ratio: 1:1 mixtures of methyl acetate and chloroform give more methane plus methyl chloride than do mixtures containing 80 mole % of carbon tetrachloride. Two unreactive solvents, 1-octene and methyl benzoate, give only about 30% of methane plus methyl chloride, suggesting that here about 10% of Reaction (4) occurs at the expense of reaction (1).

Although the quantities of ethane found are erratic (see experimental part), the higher ethane yields in methyl benzoate and toluene may be significant, in which case *removal of methyl radicals from the solvent* is indicated.

Relative Reactivities of Solvents toward Free Radicals.—Table IV summarizes the results on the relative reactivities of solvents with the radicals from decomposing acetyl peroxide, as measured in Table III. The last three columns in Table IV give the relative reactivities of some of these solvents toward the long-chain primary alkyl radicals in polymerizing ethylene and the substituted benzyl radicals in polymerizing styrene. The results in each column are referred to carbon tetrachloride as unity. Although acetone and toluene are only 0.001 to 0.01 as reactive as carbon tetrachloride toward the long alkyl and substituted benzyl radicals, they are relatively much more reactive toward the radicals from acetyl peroxide. The contrast with cyclohexane and methyl acetate is even more striking, these solvents being considerably *more* reactive than carbon tetrachloride toward the acetyl peroxide radicals, much less reactive toward the other radicals. Chloroform is much less reactive than carbon tetrachloride toward long benzyl radicals, equally reactive toward long alkyl radicals and more reactive toward the radicals from acetyl peroxide.

TABLE IV

RELATIVE REACTIVITY OF SOLVENTS AND CARBON TETRACHLORIDE TOWARD VARIOUS FREE RADICALS

Solvent	Radical from Ac_2O_2 (100°)	Radical in polymerizing Ethylene[a] (70°)	Styrene[b] (60°)	Styrene[b] (100°)
Benzene	0.039	0.002	0.0002	0.001
Methyl benzoate	0.062	....	....	....
Acetone	0.40	0.013	0.0055	....
Toluene	0.75	....	0.0014	0.0036
Carbon tetrachloride	1.00	1.00	1.00	1.00
Octene-1	3.2	....	....	....
Cyclohexane	4.8	....	0.00026	0.0009
Chloroform	11.1	1.0[c]	0.0055	....
Methyl acetate	21	0.003[d]	0.003[e]	0.004[e]

[a] Reference 4a, taking the transfer constant for long radicals with carbon tetrachloride as 3.2 (ref. 4b). [b] Refs. 3a,c,d. [c] Unpublished work by J. R. Little and G. S. Mills in this Laboratory. [d] Ethyl acetate. [e] Methyl chloroacetate.

The difference between the long radicals is unaccounted for except by possible steric effects, and here there is no obvious abnormality in the behavior of the acetyl peroxide radicals.

The contrast between the relative reactivities of these solvents with long radicals and with the radicals from acetyl peroxide forces us to one of two conclusions: (1) methyl radicals behave *much* differently from other hydrocarbon radicals, or (2) in the decomposition of acetyl peroxide, *we are dealing partly or wholly with acetate radicals which decarboxylate as they react.* We favor the latter explanation for the following reasons: (1) The yields of methane plus methyl chloride are highest with the most reactive solvents. This relation is expected if we are concerned with acetate radicals which can have alternative reactions to give less volatile products, *e. g.*, acetic acid, but the relation is difficult to understand for methyl radicals formed directly from the peroxide and having no corresponding alternative. The expected alternative for methyl radicals, formation of ethane, is not particularly favored in solvents giving low yields of methane plus methyl chloride.[9] These conclusions are entirely consistent with those of Bartlett and Altschul.[10] From the evolution of carbon dioxide from benzoyl peroxide in allyl acetate, they concluded that this gas does not come from a unimolecular decomposition of the benzoate radical but may arise (a) only from some spontaneous decomposition of the peroxide or (b) only from decarboxylation of benzoate radicals during reaction with other molecules. All these considerations suggest that the solvents which by our measurements are found to be "most reactive" toward the radicals from acetyl peroxide are those which are best able to decarboxylate acetoxyl radicals with simultaneous liberation of methane or methyl chloride. (2) Since acetate radicals would be expected to prefer reaction with electron-donor solvents,[11] the low reactivity of carbon tetrachloride is accounted for. (3) Acetate radicals should be more stabilized through resonance than methyl radicals. (4) Although the neophyl radical[12] when prepared by the decomposition of β-phenylisovaleryl peroxide does not rearrange, the neophyl radicals which apparently occur in the reaction of neophyl chloride with either phenylmagnesium bromide or butylmagnesium chloride in the presence of 2–3 mole % cobaltous chloride,[13] or in the peroxide-catalyzed chain decomposition of β-phenylisovaleraldehyde,[14] and which cannot be protected by a carboxyl group, show partial rearrangement. (5) Kharasch and Urry[15] have reported different behaviors of propyl radicals prepared from peroxide decomposition and from Grignard reactions.

Summary

The thermal decomposition of dilute solutions of acetyl peroxide in single and mixed solvents was studied at 60–100°. Investigation of both gaseous and liquid products in a single large run in carbon tetrachloride accounted for 95% of the methyl residues and 87% of the the theoretical carbon dioxide.

The other, small scale, experiments were concerned mostly with the ratio of methane to methyl chloride formed. With carbon tetrachloride as the only solvent, some methane was formed but the proportions of methane and methyl chloride were not reproducible unless a very small proportion of acetic anhydride was added. From the much larger methane:methyl chloride ratios obtained from mixtures of carbon tetrachloride with benzene, toluene, cyclohexane, 1-octene, acetone, methyl acetate, methyl benzoate, or chloroform (which yields mostly methane and little methyl chloride by itself), the relative reactivities of these solvents toward the radicals in decomposing acetyl peroxide were determined. These relative reactivities are so different from those of the same solvents toward the long-chain alkyl and substituted benzyl radicals in polymerizing ethylene and styrene that one of two conclusions is indicated: either (1) methyl radicals behave much differently than other hydrocarbon radicals or else (2), the preferred alternative, the decomposition of acetyl peroxide yields acetate radicals which decarboxylate as they react.

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[9] The lower over-all yields of gas from "less reactive" solvents may also possibly be due to spontaneous formation of more acetate and fewer methyl radicals in these solvents.

[10] Bartlett and Altschul, THIS JOURNAL, **67**, 812 (1945).

[11] Walling, *ibid.*, **70**, 2561 (1948).

[12] S. Winstein, private communication.

[13] Urry and Kharasch, THIS JOURNAL, **66**, 1438 (1944).

[14] Winstein and Seubold, *ibid.*, **69**, 2916 (1947).

[15] Kharasch and Urry, *J. Org. Chem.*, **13**, 101 (1948).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Anisotropy of Dimethyl Terephthalate and Polyethylene Terephthalate

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The problem of evaluating molecular orientation in a substantially amorphous polymer appears to be susceptible of attack by the method of magnetic anisotropy. The method in essence is to determine the anisotropy of the monomer, or of the repeating unit, as may be possible from magnetic and X-ray measurements on relatively simple compounds, and then to interpret the anisotropy of the polymer in terms of specific orientation of the molecular magnetic axes.

Polyethylene terephthalate is promising for this kind of study because of the aromatic groups present in the chain. In the work described below, magnetic susceptibility and anisotropy measurements have been made on the polymer in various stages of molecular orientation and under various conditions of heat treatment. Measurements have also been made on dimethyl terephthalate as the nearest analog to the repeating unit in the polymer.

Experimental Part

Magnetic Measurements.—Susceptibility measurements were made by the Gouy method according to standard procedures.

Anisotropy measurements were made mostly by the second "spin" method of Krishnan, although some measurements were made by his first "oscillation" method. The apparatus, which is the same for both methods, will be described in detail.[3]

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[3] Krishnan, Guha and Banerjee, *Phil. Trans. Roy. Soc.* (*London*), **A231**, 235 (1933); **A234**, 265 (1935).